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Application of Proton Exchange Membrane Fuel Cell for Lift Trucks

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Abstract

In this study a general PEMFC (Proton Exchange Membrane Fuel Cell) model has been developed to take into account the effect of pressure losses, water crossovers, humidity aspects and voltage over potentials in the cells. The model is zero dimensional and it is assumed to be steady state. The effect of concentration loss is neglected while the effect of activation and ohmic losses is investigated in the system. Some semi-empirical equations are required to predict the amount of exchange current density for calculation of ohmic loss and water diffusion coefficient through membrane. These equations are applied in order to account for water back diffusion. Further Membrane water content is assumed to be a linear function of thickness.

PEM fuel cell is working at rather low operating conditions which makes it suitable for the automotive systems. In this paper motive power part of a lift truck has been investigated thermodynamically. The system includes a compressor, an air humidifier, set of heat exchangers and a stack which together build up the anode circuit, the cathode circuit and the cooling loop. Since fuel humidification is carried out via water cross over from cathode to anode, there is no humidifier in the anode side. The electricity needed for auxiliary components is produced by the stack. The system is set at different electrical powers. In this paper several issues are discussed; voltage losses, system efficiency as well as electrical power at different operating conditions.

Key words: PEMFC, fuel cell, anode recirculation, ohmic loss, activation loss, concentration loss, exchange current density, back diffusion

Nomenclature

V_{cell}	cell average voltage (V)	k_c	cathode reaction rate
E	theoretical voltage (V)	r_{ohmic}	ohmic resistance (Ωcm^2)
E^0	open circuit voltage (V)	r_{el}	electrical resistance (Ωcm^2)
ΔG_f^0	change in Gibbs free energy (J/molK)	r_{ion}	ionic resistance (Ωcm^2)
n_e	number of electrons transferred per mole of fuel ($\frac{mol-e^-}{mol-fuel}$)	t_m	membrane thickness (cm)
n_{el}	number of electrons in the rate determining step of the reaction	C_1	constant
F	Faraday's constant (C/mol)	C_2	constant
R	Estefan-Boltzmann constant (J/molK)	a_w	water vapour activity
T	temperature (°C)	$T_{c,outer}$	coolant inlet temperature of the outer loop (°C)
a_{H_2}	hydrogen activity	a_w	water vapour activity
a_{O_2}	oxygen activity	Greek letters	
a_{H_2O}	water activity	η_{act}	activation overpotential (V)
i	current density (A/cm ²)	η_{ohm}	ohmic overpotential (V)
i_n	internal current density (A/cm ²)	η_{conc}	concentration overpotential (V)
i_0	exchange current density (A/cm ²)	α_a	anode transfer coefficient
$i_{0,a}$	anode exchange current density (A/cm ²)	α_c	cathode transfer coefficient
$i_{0,c}$	cathode exchange current density (A/cm ²)	β	symmetry factor
k_a	anode reaction rate	λ	membrane water content

Introduction

Due to negative consequences of using fossil fuels in power generation like, finite source of energy and global warming finding an alternative energy source is inevitable. During the past decade, fuel cells have received more attention and appear to have the potential to become the power source of future. Among different types of fuel cells, PEM fuel cells seem to have the capacity to be used in automotive systems because of some desirable properties, such as a low operating temperature, which provide the possibility of using cheaper components in the system. However, lack of a hydrogen infrastructure is considered the biggest obstacle to the introduction of fuel cell vehicles and due to its low temperature operation no internal reforming can take place and only pure hydrogen can be used as a fuel. Today PEM fuel cell automotive systems are too expensive for wide-spread marketing. These systems still need some improvement so that they can compete with internal combustion engines. The fuel cell system typically involves the following subsystems: oxidant supply, fuel supply, heat management, water management, power conditioning, instrumentation and controls.

There are two distinct approaches that may be taken when modelling fuel cell systems. The first is modelling the details of a single stack and using the operating conditions to determine the current-voltage curve and the second one is modelling the fuel cell system based on voltage-current output for existing fuel cells and developing models for auxiliary components. Very little attention has been paid to optimising the entire plant system to

make the fuel cell system work efficiently. In order to have a comprehensive understanding of a fuel cell, one needs to look at its operation in the system. Modelling a fuel cell stack alone is not very advantageous. In order to investigate and optimise a fuel cell system, it is necessary to develop a comprehensive model of the stack.

There are many articles in the literature which have focused on numerical modelling of the stack and the detailed phenomena which occur in it. Papers [1] to [4] developed mathematical models based on analytical approaches. Papers [5] and [6] provide a discussion of the polarization curve in PEMFC. In [7] some key parameters estimation for the polarization curve was proposed. Other papers have discussed electrolyte properties and water diffusion phenomena in the stack. In [8] a transient analysis of water transport in a PEM fuel cell was studied in theory. In [9] an isothermal, one-dimensional, steady-state model for PEMFC was presented with a 117 Nafion as a membrane. Other researchers have taken the second approach, incorporating PEM fuel cell voltage–current density curves for existing fuel cells into a system model to examine fuel cell system performance in automotive applications [10]–[12].

In this paper a simple but general model for PEMFC is developed, which is zero dimensional and steady state. The polarization curve of the stack captures the experimental data very well. The model is applied to a 14 kw fork-lift truck power system. The thermodynamic efficiency and net power of the system is calculated for different operating conditions. The results are then validated against experimental data.

1. Methodology

In this study the thermodynamic analysis of PEMFC for a fuel cell automotive system was investigated. The conditions were assumed to be steady-state. A zero-dimensional PEMFC model was developed and is presented here. This model was built up in an in-house software, called DNA (dynamic network analysis), which is FORTRAN based. The equations used for modelling were either analytical or semi-empirical and were taken from the literature. The accuracy of the theoretical results was validated against experimental data and the I-V curve produced by this model fit very well with the corresponding experimental data. The fuel cell stack contains 110 cells with the cell area equal to 285.88 cm^2 . The operating temperature of the stack was 60-80°C and the maximum power which could be produced was equal to 20.4 kw. The advantage of this model is that it can be used for all types of PEMFC stacks by replacing some parameters, as explained in detail in the following sections.

2. System description

Figure 1, shows the schematic of the fuel cell system analysed in this study. The system includes a compressor, an air humidifier, a set of heat exchangers and a stack, which together build up the cathode circuit, the anode circuit and the cooling loop. On the cathode side, air is compressed, pre-cooled and humidified before entering the cathode side of the stack at a pressure less than 2 bar and a temperature around 60°C. The fuel used on the anode side is pure hydrogen which is assumed to be pressurized and stored in a vessel. The amount of hydrogen will be regulated by using a valve just after the vessel. For the sake of simplicity this valve is not shown in the figure. Hydrogen with a pressure less than 2.2 bar and temperature around 60°C enters the anode side of the

stack. Since all the fuel cannot be consumed inside the stack the rest will be collected and returned to the anode stream via a recirculation pump. To prevent dehydration of the membrane, air and fuel must be humidified. On the air side there is a humidifier which uses some of the water vapour from the cathode outlet to humidify the inlet air. The relative humidity of the air prior to stack is set to 95% in the calculations; although other values can be chosen. On the fuel side there is no humidifier and the fuel can reach the desired humidity by means of the water cross-over effect through the membrane from cathode to anode. Depending on stack power output, anode inlet humidity is between 91 to 100%. This aspect is revisited later in the paper.

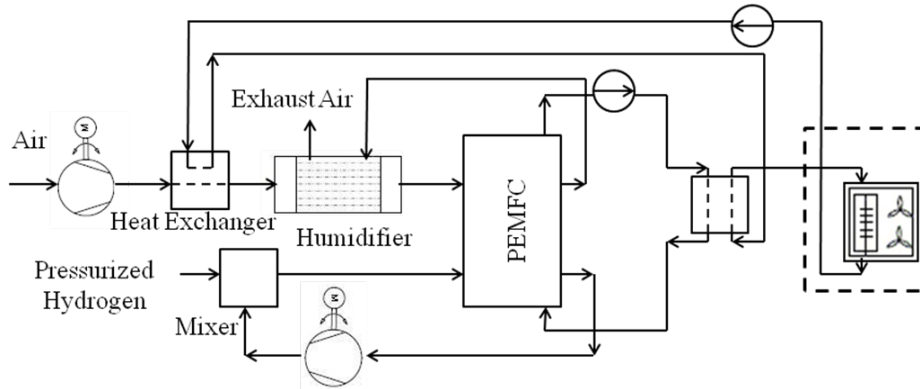


Figure1. Fuel cell system layout

For thermal management, two separate cooling circuits are used, denoted as the inner and outer loops. In both loops, water is used as a coolant, although other coolants such as ethylene glycol can also be used. The inner loop is used for stack cooling and the water keeps the stack temperature around 70°C. The heat rejected from the stack via the coolant in the inner loop is transferred to the water in the outer loop with a working temperature around 50-60°C and the waste heat in the outer loop is rejected to ambient air by fan cooling.

3. Fundamental equations

The average cell voltage of a fuel cell is defined by an analytical expression:

$$V_{cell} = E - \eta_{act} - \eta_{ohmic} - \eta_{conc} \quad (1)$$

In this study η_{act} and η_{ohmic} are discussed as described in the following sections, while the effect of η_{conc} is neglected. Theoretical voltage is usually expressed by the Nernst equation [13]:

$$E = \frac{-\Delta G_f^0}{n_e F} + \frac{RT}{n_e F} \ln \left(\frac{a_{H_2} a_{O_2}^{-0.5}}{a_{H_2O}} \right) \quad (2)$$

where a is the activity of the species. By assuming the gases are ideal, the activity of the gases is equal to their partial pressure and the activity of liquid water is equal to 1. n_e is the number of electrons transferred per mole of fuel which here is hydrogen. Therefore $n_e = 2$. ΔG_f^0 which is the change in Gibbs free energy for the reaction below, is calculated at standard pressure but is still a function of temperature.

$$\Delta G_f^0 = (G_f^0)_{H_2O} - (G_f^0)_{H_2} - \frac{1}{2} (G_f^0)_{O_2} \quad (3)$$

Due to the low temperature gradient (less than 10°C between inlet reactants and outlet products of the stack), the outlet temperature is applied to evaluate this parameter.

3.1. Activation overpotential:

Activation overpotential is the voltage required to overcome the activation energy of the chemical reaction and this is dominant at low current densities. To evaluate the activation loss, the well-known Butler-Volmer equation is used to derive the relationship between activation loss and current density. The cell total activation loss is equal to the sum of anode and cathode contributions. In order to take into account the potential caused by fuel crossover and electrons passing through the electrolyte, the internal current density is added to the actual current density which its effect is more significant in the case of low temperature fuel cell compared high temperature fuel cells. In this paper the value for i_n is assumed to be equal to 0.002 A/cm² [14].

$$\eta_{act} = \eta_{act,c} + \eta_{act,a} = \frac{R.T}{\alpha_c.F} \ln\left(\frac{i + i_n}{i_{0,c}}\right) + \frac{R.T}{\alpha_a.F} \ln\left(\frac{i + i_n}{i_{0,a}}\right) \quad (4)$$

$$\alpha_a = \beta \cdot n_{el} \quad (5)$$

$$\alpha_c = (1-\beta) \cdot n_{el} \quad (6)$$

The symmetry factor, $\beta = 0.5$ is chosen, n_e is equal to 4 for anode and 1 for cathode, see [7]. Another important issue for the estimation of activation loss is i_0 , exchange current density, which is the rate constant for electrochemical reactions and is a function of temperature, catalyst loading and catalyst specific surface area [13]. Both analytical and experimental methods for evaluating this parameter can be found in the literature. However, the analytical expression is chosen here [15], which predicts the value of the exchange current density at the anode and cathode separately. Since the amount of activation loss on the cathode side is significantly higher than the anode side, this term for anode side in equation (4) is neglected.

$$i_{0,a} = n_{el} \cdot F \cdot k_a \cdot \exp\left[\frac{(1-\beta) \cdot n_{el} \cdot F \cdot E^0}{R.T}\right] \quad (7)$$

$$i_{0,c} = n_{el} \cdot F \cdot k_c \cdot \exp\left[\frac{-\beta \cdot n_{el} \cdot F \cdot E^0}{R.T}\right] \quad (8)$$

3.2. Ohmic overpotential:

Ohmic overpotential is the sum of the ionic resistance of the electrolyte and the electrical resistance of the bipolar plate and the other electrical parts of the stack.

$$r_{ohmic} = r_{el} + r_{ion} \quad (9)$$

Since electrical resistance is much less than ionic resistance, this value is neglected in this study. An analytical expression suggested by [7] is applied in the calculation of ionic resistance with some modifications. This equation was based on an analysis of published data related to different cells, all with the Nafion 117. In this study, C_1 and C_2 are adjusted when calibrating the electrochemical model against the data available from the experimental polarization curve. The membrane thickness is equal to 0.183 mm [13].

$$r_{ion} = \frac{C_1 \cdot [1 + 0.03 \cdot i + 0.062 \cdot \left(\frac{T}{303}\right)^2 \cdot i^{2.5}]}{(\lambda - 0.634 - 3 \cdot i) \cdot \exp[C_2 \cdot ((T - 303)/T)]} \cdot t_m \quad (10)$$

Membrane water content, λ is considered as the mean value of anode and cathode water content.

4. Water cross over

The water content in the polymer electrolyte plays a significant role in PEMFC stack lifetime and the ionic resistance of the membrane. Low humidification in the membrane causes a rapid increase in ionic resistance and high humidification will cause too much liquid water to overflow into the reactant channels and fill the pores in the electrodes. In order for the membrane to have high ionic conductivity it should be fully hydrated. Hydration can be achieved by the humidification of the gases, or by designing the fuel cell to allow product water to hydrate the membrane [13]. Membrane water content at the electrode/membrane interface can be defined by following expression [13]:

$$\lambda = 0.043 + 17.18 a_w - 39.85 a_w^2 + 36 a_w^3 \quad (11)$$

which a_w is water vapor activity and is defined by [13]:

$$a_w = \frac{P_w}{P_{sat}} \quad (12)$$

where $a_w < 1$. Generally diffusion of water in the polymer electrolyte is expressed in two terms, one is the effect of electro osmotic drag which moves the water from anode to the cathode side through membrane and when the water is produced in cathode side a part of it travels from cathode to anode which is called water back-diffusion.

Water management of the membrane is a challenging issue. Normally the amount of water produced on the cathode side is much greater than the amount of water traveling from the anode to the cathode side. This means that a considerable amount of water moves to the anode side and can be used for fuel humidification. There is then no need for a humidifier on the anode side as discussed before.

5. Parameter estimation of the polarization curve

By applying the equations mentioned above, a general PEMFC model with several constants can be constructed. These constants in this model are the reaction speed in the cathode side, k_c in equation (8), C_1 and C_2 , the constants in ionic resistance formula, in equation (10). The original values for these two constants can be found in [7] which are equal to 181.6 and 4.18 respectively. For different stacks these constants are different and must be calibrated against experimental data. This model is therefore valid for PEM stacks with different dimensions and operating conditions. The stack which is used in this study is one of the products of the Ballard Company for which the I-V curve obtained from experimental data are available. As in experiments, the same operating conditions are used to validate the results. Figure 2 shows comparison between the theoretical and experimental data for the polarization curve. As shown, the model matches the experiment

very well. In this analysis the values for k_e , C_1 and C_2 is found to be equal to 170, 15.4 and 0.415 respectively.

6. Operating conditions

The operating parameters which must be set in the program are air and fuel inlet stoichiometry, inlet pressure, pressure drop, relative humidity and operating temperature of the stack, which in fact determine the outlet temperature of the product gases. In order to obtain the maximum service life and stack efficiency, Ballard recommends the operating conditions within which the stack should operate [18]. In current calculations these operating conditions are applied.

Due to the chemical reactions which occur inside the stack there is a difference between stack inlet and outlet gas conditions in terms of their temperature, pressure, humidity and molar ratio of the species. It is therefore necessary to use the mean value for some parameters in present equations. However, using the average value of inlet and outlet is not always the best choice. Therefore, a weighting parameter is defined, which can solve this problem and it is set to 0.2, implying that when deriving the mean value of a parameter, 20% of inlet and 80% of outlet conditions are used.

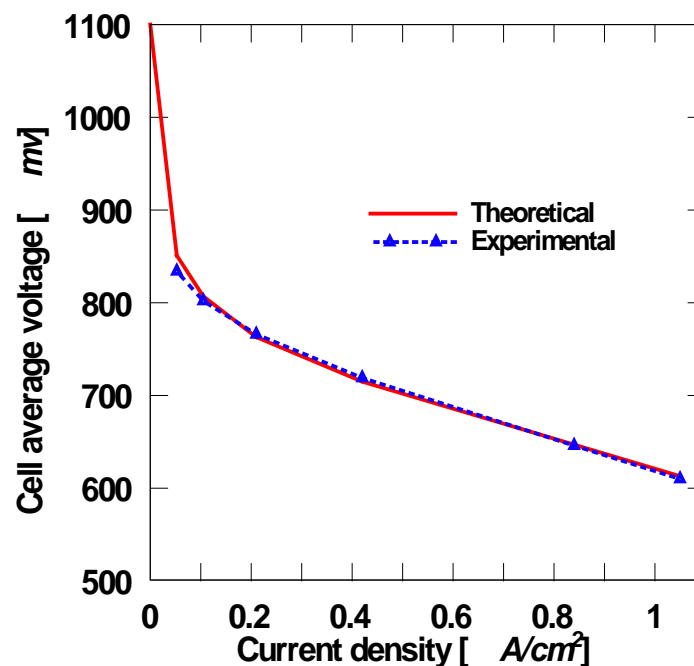


Figure 2. The comparison between theoretically and experimentally obtained polarization curve

7. Results

7.1. System sensitivity to coolant inlet temperature

As already discussed, there are two cooling circuits in the system, inner and outer. In the inner loop water inlet and outlet temperature is equal to air and fuel inlet and outlet temperatures, since the coolant, air and fuel channel are close to each other. In order to

evaluate the effect of coolant inlet temperature of the outer loop, $T_{c,outer}$ on system performance with net power output around 14 kW, the coolant outlet temperature is fixed to 68.2 °C. With changing $T_{c,outer}$ from 40 to 60 °C the coolant mass flow of the outer loop changes from 0.13 to 0.46 kg/s and the mass flow of the inner loop keeps constant at 0.44 kg/s. As is illustrated in figure 3, system efficiency and average cell voltage keep constant. It is quite obvious that system performance is not sensitive to the coolant temperature.

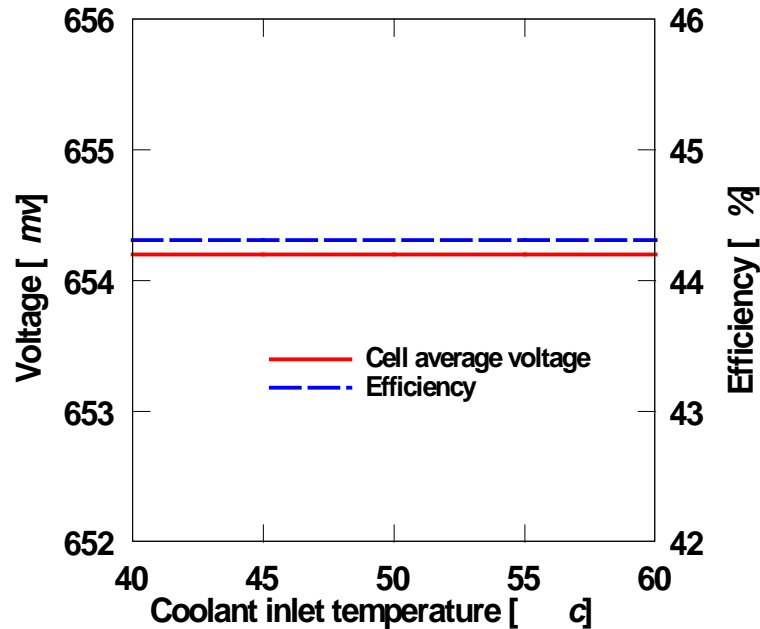


Figure. 3. The effect of $T_{c,outer}$ on system voltage and efficiency

7.2. System output versus current density

In different current densities, the fuel cell system have been run to analyse the system efficiency, power output and also the amount of heat which is generated by the stack. For the fuel cell stack, the operating conditions are applied which are already discussed above. The operating conditions of the stack are also affecting the function of the auxiliary components like the compressors efficiencies. For air side the efficiency of compressor is ranged from 14% to 39% in the calculations, depending on the air mass flow. This efficiency is the product of isentropic and mechanical efficiency and is assumed as a linear function of mass flow. Figure 4 shows that by increasing current density the power generated from the stack increases. But looking at the net power of the system it becomes clear that in the higher currents, power consumption of the auxiliary components is also higher which makes the efficiency to decrease. Another parameter which is illustrated in this figure is the power generated by the stack which is close to the stack power values and increases with current densities. This parameter is an important factor for stack cooling, because this amount of heat is dedicated to the coolant via a heat exchanger in order for the stack temperature to be kept constant.

7.3. System sensitivity to air and fuel stoichiometry

Figure 5, demonstrates the effect of air and fuel stoichiometry on system performance. To study the system sensitivity to stoichiometry, the operating conditions of the base case with 14 kW net power output is used. First air stoichiometry is fixed on 1.8 and fuel stoichiometry is changed from 1 to 2.2 and then in order to analyse the effect of air stoichiometry, fuel

stoichiometry is fixed on 1.6. As it is shown in the figure, fuel stoichiometry is not a critical issue from system performance view and it seems that cell voltage and system efficiency is more sensitive to air stoichiometry. The cell average voltage increases by increasing air stoichiometry, while efficiency decreases significantly. This is because of higher effect of compressor on the higher air mass flow.

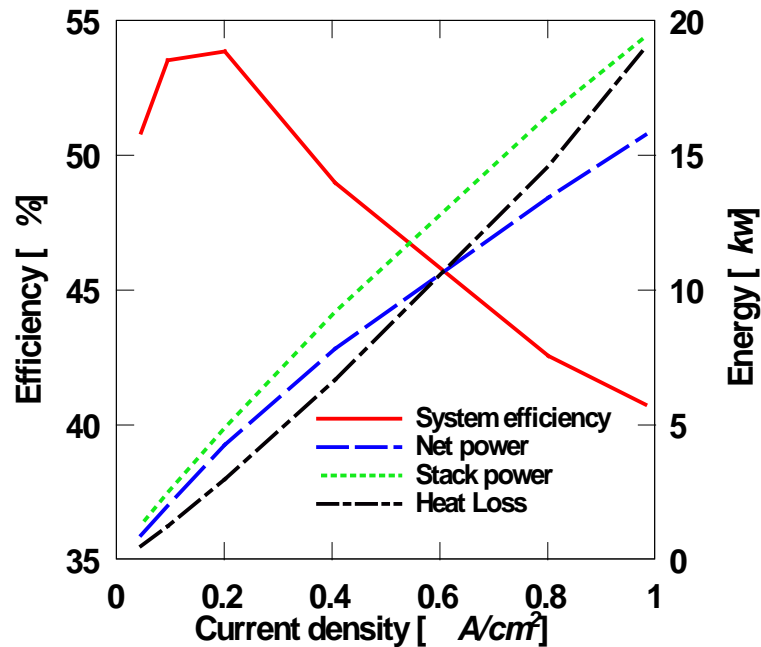


Figure 4. Efficiency and power versus current density

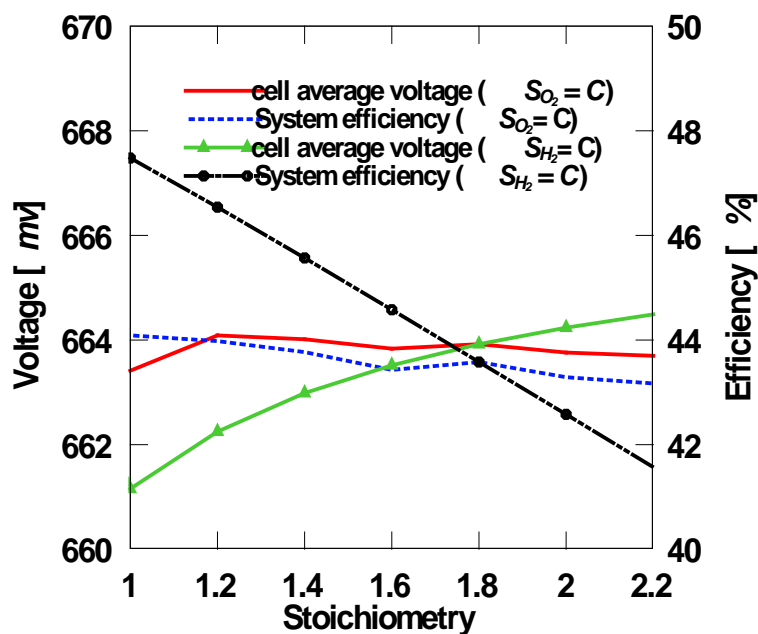


Figure 5. Sensitivity of voltage and efficiency versus stoichiometry.

7.4. Anode inlet pressure effect

For the base case with cathode inlet pressure equal to 1.8 bar, system performance with hydrogen inlet pressure ranged from 1.6 to 3 have been analysed. But generally lower

pressure in the anode side than cathode is not recommended because nitrogen cross-over rates from the cathode to the anode increase as cathode pressure increases relative to the anode pressure. Ensuring the cathode pressure is lower than the anode pressure will minimize nitrogen crossover and improve cell stability [18]. As it is seen in figure 6, higher hydrogen inlet pressure increases both voltage and efficiency. But it should be noticed that there is also limit for this pressure due to structure and sealing.

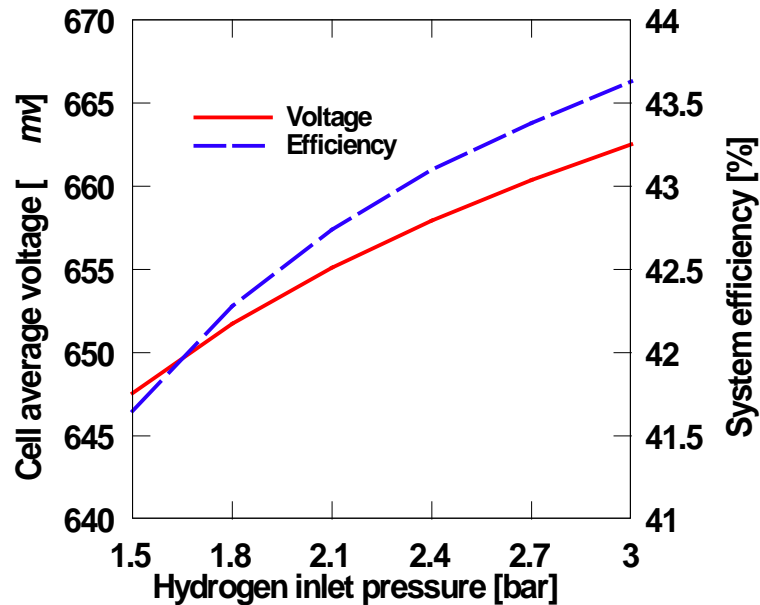


Figure 6. Anode inlet pressure effect on system performance.

8. Conclusion

In this paper a general PEMFC model is developed based on theoretical analysis and semi empirical equations. There are several key parameters in the model which are defined so that theoretical I-V curve capture the experimental polarization curve very well. In this case the model has been validated against a special stack data from Ballard company. With applying this stack in the fuel cell system the following listed results have been achieved.

1. PEMFC system is not sensitive to coolant temperature.
2. In the higher current densities the amount of heat loss and the net power of the system increase, but system efficiency decreases.
3. Sensitivity of the system to air stoichiometry is much more than fuel stoichiometry.
4. In the higher inlet pressure of the fuel both system efficiency and net power increases.

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